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TECHNICAL NOTE

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ABSTRACT

The simple Hückel method was first applied to the electronic structure of the iron-porphyrin complexes by Pullman et al. [1] In this paper, their work is extended to include (a) the effect of a dipole or a point charge placed at the sixth coordination position, and (b) the effect of a nitrogen atom placed at the fifth coordination position. A set of new parameter values is used, whose estimation is made by directing special attention to their dependence on the charge distribution among the atoms.

The resulting charge distribution for ferro-porphyrin seems to be reasonable. The fact that the position of the Soret peak is insensitive to the sixth ligand can be understood from the resulting orbital energy levels.

The difficulty of finding a reasonable charge distribution for ferri--porphyrin is discussed.

1. INTRODUCTION

One of the most interesting chemical properties of Fe-porphyrin complexes is the existence of "high-spin" and "low-spin" states. For example, the number of unpaired spins in Hb - H_2O and Hi - H_2O is 4 and 5 respectively, while that in Hb - O_2 and Hi - OH^- is 0 and 1 respectively.

Another interesting feature is their spectra. All these complexes show an extremely strong band, called the Soret band, at 390 ~ 430 mμ. The position of the peak does not change very much for Hb - H_2O, Hb - O_2 and even for metal-free porphins.

The complexes are known to play very important roles in oxidative and reductive reactions in biological systems. It has been pointed out that this redox power is closely related to the orbital energies of the highest occupied and the lowest unoccupied molecular orbitals. [2]

It is very difficult to give a theoretical interpretation of these phenomena from first principles. And it is even more difficult to explain the oxygen--uptake power of haemoglobin. However, it is clear that one of the most fundamental pieces of knowledge about this molecule is its electronic structure.

We use the simple Hückel method in this work not because it is adequate for our purposes, but because it is simple enough to be easily applied to complicated systems such as the iron-porphyrin complexes.

The simple Hückel method was first applied to the iron-porphyrin complexes by Pullman, Spanjaard and Berthier. [1,3] Their calculations are extended in this work to include (a) the effect of a dipole or a point charge placed at the sixth coordination position, and (b) the effect of a nitrogen atom placed at the fifth coordination position. We also introduce new parameter values, whose estimation is made by directing special attention to their dependence on the charge distribution among the atoms.

In Pullman and others' work, [1,3] it was assumed that in the high--spin complexes the 3d electrons of the iron atom do not participate in the bonding between Fe and the porphin ring, while in the low-spin complexes, they do. The calculated molecular orbital energies differed considerably for these two types of complexes. The work, therefore, suggested that when a complex changes its spin state, there are drastic changes both in the charac-

ter and in the energy of the molecular orbitals involving the 3d orbitals. This may well be true, but the specific assumption mentioned above is rather artificial. Here we lift this assumption. Changes in molecular orbitals will be brought about through the dependence of the parameters on the charge distributions which are different for the high- and low-spin state.

2.   THE MODEL

All the peripheral substituents of the porphyrin ring are neglected so that the system under consideration contains 20 C's, 4 N's, and one Fe in the molecular plane (cf. Fig. 1), and one N under the Fe atom - this will be denoted hereafter N' . The assumed distances between the atoms are the following: Fe - N 1.80 A, N - C' 1.38 A, C' - C and C' - C" 1.4 A, Fe - N' 2.10 A . The bond angle $\angle C'NC'$ of 108° is also assumed. These figures are fairly close to the observed ones for nickel ethioporphyrin [4] and myoglobin. [5]

The ligand at the sixth coordination position apparently determines the spin state of the system. We replace this ligand by a dipole or a point charge and investigate its effect. A dipole with its axis perpendicular to the molecular plane or a point charge is thus placed above the Fe atom at the distance of 2.06 A . The system has the symmetry C_{4v} .

The system is so large that only the bonds between Fe and four surrounding N's are considered for the σ part; also the possible π bonding between Fe and N' is neglected. With all these simplifications, there are 42 electrons (one each from C, three each from N, 8 from Fe and 2 from N') for the ferrous complex and 41 electrons for the ferric complex. To describe them, we use the following 38 atomic orbitals: one $2p\pi$ of each C, one $2p\pi$ and one sp^2 hybridized σ of each N, five 3d, one 4s and three 4p of Fe and one sp^2 hybridized orbital of N' pointing to Fe .

3. METHOD OF CALCULATION

Our model has the symmetry of C_{4v} but if we disregard the point charge or dipole at the sixth coordination position and the N' atom at the fifth coordination position, the symmetry is D_{4h}. It is more convenient to name some of the molecular orbitals after the irreducible representations of the group D_{4h}. The names of the irreducible representations of the groups D_{4h} and C_{4v} and the relation between them can be seen in Table I.

TABLE I   Irreducible representations of the groups D_{4h} and C_{4v}.

D_{4h}	A_{1g} A_{2u}	B_{1g} B_{2u}	A_{2g} A_{1u}	B_{2g} B_{1u}	E_g E_u
C_{4v}	A_1	B_1	A_2	B_2	E

Putting aside the orbital of N', we form linear combinations of the 37 atomic orbitals available. The linear combinations form bases for the irreducible representations of D_{4h}. These are called symmetry orbitals and explicit forms are given in Appendix I. The irreducible representations which appear and number of linearly independent functions belonging to these follow: A_{1u} (2), A_{2u} (5), B_{1u} (3), B_{2u} (3), E_g (7), A_{1g}(3), B_{1g}(2), B_{2g}(1) and E_u (2).

When the atom N' and/or a point charge or a point dipole are considered, we have A_1 (9) instead of A_{1g} (3) and A_{2u} (5) and an sp^2 hybrid of N' pointing to the Fe atom. Off-diagonal elements between B_{1g} and B_{2u}, B_{2g} and B_{1u}, E_g and E_u will be zero under the approximations employed in the present calculations. (This will be explained in the next section). Even in the general case we shall keep the symmetry notation of D_{4h} except for A_{1g} and A_{2u}.

Thus we have expressed the symmetry orbitals in terms of atomic orbitals. In order to know how much these symmetry orbitals mix to give molecular orbitals, we have to set up and solve the secular equations.

Integrals which appear in the secular equations can be reduced to those involving atomic orbitals. In the simple Hückel theory, they are the Coulomb integrals α, the resonance integrals β and the overlap integrals

S . They are defined as

$$\alpha_p = \int \chi_p^*(1) \, H_{eff}(1) \, \chi_p(1) \, dv_1, \qquad (3.1)$$

$$\beta_{pq} = \int \chi_p^*(1) \, H_{eff}(1) \, \chi_q(1) \, dv_1, \qquad (3.2)$$

$$S_{pq} = \int \chi_p^*(1) \, \chi_q(1) \, dv_1, \qquad (3.3)$$

where χ_p and χ_q are the atomic orbitals. The total Hamiltonian is assumed to be a sum of one-electron effective Hamiltonians H_{eff}:

$$H = \sum_i H_{eff}(i). \qquad (3.4)$$

The one-electron effective Hamiltonian $H_{eff}(i)$ may be considered to have the following form:

$$H_{eff}(i) = -\frac{1}{2} \Delta_i + \sum_a v_a(i), \qquad (3.5)$$

where v_a is the effective potential due to atom a .

The Coulomb integral α_p for an atomic orbital χ_p centred on the atom a can be split into two parts, α_p' and α_p'' :

$$\alpha_p = \int \chi_p^* \left(-\frac{1}{2} \Delta + v_a \right) \chi_p \, dv + \sum_{b \neq a} \int \chi_p^* \, v_b \chi_p \, dv \qquad (3.6)$$

$$= \alpha_p' + \alpha_p'' .$$

The first term α_p' may be equated to a suitable valence-state ionization potential for occupied atomic orbitals (e.g. $2p\pi$ of C , N and 3d of Fe^{++}) or to an electron affinity for empty atomic orbitals (e.g 4s and 4p of Fe^{++}). The second term α_p'' is neglected unless atom b has an appreciable formal charge. When the atom b does have a formal charge, Z_b , the term is evaluated by assuming that a point charge, Z_b , is situated at the nucleus b .

The resonance integrals β_{pq} are estimated by a slightly modified Wolfsberg-Helmholz approximation,[6] namely

$$\beta_{pq} = S_{pq} \left\{ K \, \frac{\alpha_p' + \alpha_q'}{2} + \frac{\alpha_p'' + \alpha_q''}{2} \right\}, \qquad (3.7)$$

where $K = 2$ for π bonds and 1.67 for σ bonds. The basis of this approximation is not quite clear but it is certainly most convenient in reducing the number of unknown parameters. The modification we made consists in separating off the electrostatic part α_p'' from α_p'. This is made in order to fulfill the requirement that the resulting orbital-energy differences should not change, if we change the zero point of the energy by adding a constant potential to the Hamiltonian.

The values of the overlap integrals can be evaluated without too much difficulty, at least in principle.

It should be noted that all the parameters α, β and S depend on the formal charge which the atoms carry. This necessitates the use of the method of trial and error which goes as follows. We first assume a charge distribution and determine the parameters. Then we obtain the molecular orbitals and orbital energies, and thus we are led to a plausible electron configuration. Analyzing the wave function of this electron configuration, we obtain a resulting charge distribution. If this is close to the starting charge distribution, we can stop there. If the resulting electron distribution differs from the starting one, we have to start again assuming a more appropriate charge distribution. This is a requirement of self-consistency in charge distribution which seems to be quite important in dealing with very hetero-polar systems like metal-porphyrine complexes.

The potentials due to a point charge (charge Ze), a dipole (moment μ with the axis on the z axis) and an axial quadrupole (moment Q^* with the axis perpendicular to the z axis and parallel to the y axis) placed at the distance R from the origin can be expressed, respectively, in the polar coordinates as follows:

$$V = \sum_{k=0}^{\infty} P_k (\cos \theta) \frac{Ze}{R} \begin{cases} (r/R)^k, & r < R, \\ (R/r)^{k+1}, & r > R, \end{cases} \tag{3.8}$$

---

* The quadrupole moment is defined as

$$Q = \frac{1}{4} \int (3x^2 - r^2) \rho \, dv,$$

where ρ is a charge distribution function.

$$V = \sum_{k=0}^{\infty} P_k(\cos\theta) \frac{\mu}{R^2} \begin{cases} -(k+1)(r/R)^k, & r < R, \\ k(R/r)^{k+1}, & r > R, \end{cases} \quad (3.9)$$

$$V = \sum_{k=0}^{\infty} P_k(\cos\theta) \frac{Q}{R^3} \begin{Bmatrix} -(2k+1)(r/R)^k \\ 0 \end{Bmatrix} + \sum_{k=2}^{\infty} \left[\sqrt{\frac{(k-1)k(k+1)(k+2)}{8}} \times \right.$$

$$\left. \times P_k^2(\theta,\varphi) - \frac{k(k-1)}{2} P_k(\cos\theta) \right] \frac{Q}{R^3} \begin{cases} (r/R)^k, & r < R \\ (R/r)^{k+1}, & r > R \end{cases} \quad (3.10)$$

In the last expression $P_k^2(\theta, \varphi)$ is defined as

$$P_k^2(\theta,\varphi) = \sqrt{\frac{2\pi}{2k+1}} \left\{ Y_{k,2}(\theta,\varphi) + Y_{k,-2}(\theta,\varphi) \right\} \quad (3.11)$$

In calculating matrix elements of these potentials with respect to the s-, p- and d-type atomic orbitals, the integrals can be carried out over the angular parts easily and the resulting expressions are listed in Appendix II.

4. VALUES OF THE PARAMETERS FOR FERROUS COMPLEXES

As was explained in the previous section, our parameter values depend on the charge distribution we assume.

The choice of parameters by Spanjaard and Berthier [3] indicated that they started from a model in which all the atoms are neutral. The resulting formal-charge distributions were $Fe^{3.5+}$ porphin$^{3.5-}$ and $Fe^{1.5+}$ porphin$^{1.5-}$ for low- and high-spin ferrous complexes. In view of these results, we start with a model in which the formal-charge distribution is $Fe^{2.0+} N^{0.5-}$, all carbon atoms being considered as neutral.

4.1. Valence-state ionization potential and electron affinity

The first term a_p' of the parameter a (cf. (3.6)) is equated to a suitable valence-state ionization potential for occupied atomic orbitals or to an electron affinity for unoccupied atomic orbitals. The values of these used in the present calculation are collected in Table II.

TABLE II Valence-state ionization potentials and electron affinities (in eV).

Ionization potential I			Electron affinity A		
Atom	Orbital	I	Atom	Orbital	A
C	$2p\pi$	11.42 [1]	Fe^{2+}	4s	16.18 [3]
N'	$2p\pi$	14.26 [2]	Fe^{2+}	4p	11.41 [3]
N''	σ	18.67 [2]			
$N^{0.5-}$	$2p\pi$	7.79 [2]			
$N^{0.5-}$	σ	12.08 [2]			
Fe^{2+}	3d	30.65 [3]			

[1] The valence state is assumed to be the tetra-valent sp^3 state. The value is taken from the paper by H.O. Pritchard and H.A. Skinner, Chem. Rev. 55, 745 (1955).

[2] For nitrogen, the valence state is assumed to be a mixture of V_3 s^2p^3 with factor 1/3 and V_3 sp^4 with factor 2/3. In estimating I for the sp^2 hybridized σ, I of 2s for V_3 s^2p^3 is assumed to be the same as that for V_3 sp^4. Numerical values are taken from Pritchard and Skinner's paper.

For $N^{0.5-}$, an additional assumption is necessary. It is observed that the ionization potential of 2p electrons for N^-, N and N^+ is a linear function of the ionicity of the atom. Thus it is assumed that

$$I(N^{0.5-}) = \frac{1}{2} \{ I(N) + I(N^-) \} .$$

[3] $I(Fe^{2+} 3d) = E(3d^5) - E(3d^6) ,$

$A(Fe^{2+} 4s) = E(3d^6) - E(3d^6 4s) ,$

$A(Fe^{2+} 4p) = E(3d^6) - E(3d^6 4p) .$

Atomic term values are found in the book by C.E. Moore; "Atomic Energy Levels", National Bureau of Standards, Vol. II (1952).

4.2. Contribution to α from the other atoms
carrying a formal charge

The second term α_p'' is estimated by assuming the point charges Ze ($Z = +2$ for Fe, and -0.5 for each of four N) are located on the nuclei. For C , for example, we have

$$\alpha_C'' = 2 \int \frac{|2p\pi_C(r)|^2}{|r - R_{Fe}|} \, dv - \int \frac{|2p\pi_C(r)|^2}{|r - R_N|} \, dv -$$
$$- \int \frac{|2p\pi_C(r)|^2}{|r - R_N'|} \, dv \tag{4.1}$$

where R_N and R_N' are the position vectors of the nitrogen nuclei nearer and farther to the C atom under consideration, respectively. Each term in the right hand side of (4.1) is a so-called nuclear attraction integral.

For the atomic orbitals used in estimating these integrals, for example $2p\pi_C$, in (4.1), we take the Slater orbitals. The orbital exponents δ are assumed as follows:

$$
\begin{aligned}
\delta(N) &= 1.95 , \\
\delta(C) &= 1.625 , \\
\delta(Fe\,3d) &= 2.08 , \\
\delta(Fe\,4s) &= \delta(Fe\,4p) = 1.01 .
\end{aligned}
\tag{4.2}
$$

For N and C , the values of the nuclear attraction integrals are obtained by interpolation of the table by Kotani et al. [7] To calculate the nuclear attraction integrals which involve Fe atomic orbitals, the formulae given in Appendix II are used, where the values of the incomplete Γ function are interpolated from Pearson's table. [8]

4.3. Values of Coulomb integrals α.

The values of α_p', α_p'' as well as α_p $(=\alpha_p' + \alpha_p'')$ are listed in Table III.

TABLE III   The parameter α for the model $Fe^{2+}N^{0.5-}$ (in eV).

Atom	Orbital	α'	α''	$\alpha = \alpha' + \alpha''$
$N^{0.5-}$	π	-7.79	-7.92	-15.71
$N^{0.5-}$	σ	-12.08	-11.72	-23.80
C'	π	-11.42	0.91	-10.51
C''	π	-11.42	0.44	-10.98
C	π	-11.42	0.28	-11.14
Fe^{2+}	$3d$	-30.65	15.80	-14.85
Fe^{2+}	$4s$	-16.18	13.12	-3.06
Fe^{2+}	$4p$	-11.41	13.12	1.71
N'		-18.67	-4.99	-23.66

4.4. Overlap integrals

The values of the overlap integrals (except those involving N' orbital) were calculated by Spanjaard and Berthier [3] using Slater orbitals. Those involving N' orbital, we have calculated using the same AO's.

We adopt Spanjaard and Berthier's values for the overlap integrals between C and C, and C and N. However, their values for the overlap integrals between Fe and N are modified by multiplying them by the constant factor 0.75. This factor is the ratio a/b. a is the overlap integral between the Fe^{2+} Hartree-Fock $3d\sigma$ [9] and the N sp^2 hybridized Slater orbital evaluated along the internuclear axis. b is the same integral between the Fe Slater $3d\sigma$ orbital and the N sp^2 hybridized Slater orbital.

This procedure is introduced to obtain approximate overlap integrals between Fe^{2+} and N , but is certainly a very crude one. However, it is hoped that the results of the calculations are not so sensitive to the values of the overlap integrals. The values used are given in Table IV.

TABLE IV.   Values of overlap integrals

$(C\,2p\pi\,|\,C\,2p\pi)$	0.2444
$(C\,2p\pi\,|\,N\,2p\pi)$	0.1930
$(Fe\,3d\pi\,|\,N\,2p\pi)$	0.1040
$(Fe\,4p\pi\,|\,N\,2p\pi)$	0.1297
$(Fe\,3d_{z^2}\,|\,N\,2p\sigma)$	-0.1133
$(Fe\,3d_{x^2-y^2}\,|\,N\,2p\sigma)$	0.1963
$(Fe\,4s\,|\,N\,2p\sigma)$	0.2129
$(Fe\,4p\sigma\,|\,N\,2p\sigma)$	0.2939
$(Fe\,3d_{z^2}\,|\,N')$	0.1560
$(Fe\,4s\,|\,N')$	0.2025
$(Fe\,4p\,|\,N')$	0.2976

4.5.   Resonance integrals

Resonance integrals between non-neighbours are neglected. Those between neighbours are calculated from Coulomb and overlap integrals by using the formula (3.7).

4.6. Effects of a point charge or a dipole

The cases in which a dipole of either 0.5 or 1.0 a.u., or a point charge of 1.0 a.u. is placed at the sixth coordination position are investigated.

The effects of these static fields on the Coulomb integrals $(\alpha")$ are calculated by the formulae given in Appendix II. The resonance integrals are changed accordingly (cf. (3.7)). However, direct contributions of the static fields to the resonance integrals are neglected.

In the non-oxygenated condition of haemoglobin, the water molecule is attached at the sixth coordination position, while in the oxygenated condition, the oxygen molecule is attached there.

The permanent dipole of the water molecule is known to be 0.728 a.u. (= 1.85 Debye) by experiment. Induced dipoles of the water and oxygen molecules placed at a distance of 2.01 Å from Fe are estimated to be 0.54 and 0.55 a.u., respectively. In this estimation, we must, of course, take into account the effect from the negative formal charge of 0.5 on each nitrogen atom.

Assume that we can neglect the polarization of the surroundings although this is very doubtful. Then the main part of the electrostatic interaction between the haem and the oxygen (or water) molecule may be represented by placing a dipole of 0.5 (1.0) a.u. at the sixth coordination position.

5. RESULTS AND DISCUSSION FOR FREE

PORPHIN AND FERROUS PORPHYRIN

5.1. Orbital energy and atomic population analysis

Orbital energies are tabulated in Table V, and the significant energy levels are illustrated in Figure 3. Because a comparison of the absolute energies of cases having different external fields has little meaning, the orbital energy differences are recorded with respect to the $1a_{1u}$ orbital, as shown in the figure.

For free porphin, we choose a model in which the two protons inside the porphin ring are completely screened by σ electrons. The four nitrogens contribute 6 π-electrons to the system. 26 π-electrons occupy the lowest

TABLE V   Orbital energies (in eV).

Porphin		Iron-porphyrin							
		No external field		D = 0.5 a.u.		D = 1.0 a.u.		P = -1.0 a.u.	
		$9a_1$	7.27	$9a_1$	7.73	$9a_1$	8.22	$9a_1$	14.76
		$2e_u$	5.17	$2e_u$	5.54	$2e_u$	5.90	$2e_u$	10.62
		$8a_1$	2.49	$8a_1$	2.93	$8a_1$	3.37	$8a_1$	8.88
		$3b_{1u}$	0.11	$3b_{1u}$	0.25	$3b_{1u}$	0.39	$3b_{1u}$	3.75
		$7e_g$	-0.21	$7e_g$	-0.05	$7e_g$	0.11	$7e_g$	3.57
$3b_{1u}$	-0.50	$7a_1$	-1.51	$7a_1$	-1.30	$7a_1$	-1.09	$7a_1$	2.66
$6e_g$	-0.59	$2a_{1u}$	-3.37	$2a_{1u}$	-3.25	$2a_{1u}$	-3.12	$2a_{1u}$	0.10
$4a_{2u}$	-0.71	$6e_g$	-4.62	$6e_g$	-4.44	$6e_g$	-4.25	$6e_g$	-0.71
$2a_{1u}$	-3.95	$3b_{2u}$	-6.63	$3b_{2u}$	-6.43	$3b_{2u}$	-6.22	$2b_{1g}$	-1.94
$5e_g$	-4.89	$2b_{1g}$	-8.48	$2b_{1g}$	-7.76	$2b_{1g}$	-7.04	$3b_{2u}$	-2.52
$3b_{2u}$	-6.14	$2b_{1u}$	-8.97	$2b_{1u}$	-8.86	$2b_{1u}$	-8.74	$6a_1$	-4.35
$2b_{1u}$	-9.39	$5e_g$	-10.29	$5e_g$	-10.07	$6a_1$	-9.60	$2b_{1u}$	-5.61
$4e_g$	-10.79	$6a_1$	-11.80	$6a_1$	-10.70	$5e_g$	-9.80	$5e_g$	-5.67
$3a_{2u}$	-12.47	$1a_{1u}$	-12.14	$4e_g$	-11.83	$4e_g$	-11.27	$4e_g$	-7.26
$1a_{1u}$	-12.92	$5a_1$	-12.36	$1a_{1u}$	-11.98	$1a_{1u}$	-11.81	$1b_{2g}$	-8.14
$3e_g$	-13.82	$4e_g$	-12.40	$5a_1$	-12.23	$5a_1$	-12.10	$1a_{1u}$	-8.35
$2b_{2u}$	-13.84	$3e_g$	-13.39	$3e_g$	-13.25	$3e_g$	-13.11	$5a_1$	-8.79
$2a_{2u}$	-13.86	$2b2u$	-13.76	$2b_{2u}$	-13.63	$1b_{2g}$	-13.28	$3e_g$	-9.80
$2e_g$	-14.12	$4a_1$	-14.02	$4a_1$	-13.85	$2b_{2u}$	-13.49	$2b_{2u}$	-10.20
$1b_{1u}$	-14.66	$1b_{1u}$	-14.05	$1b_{1u}$	-13.89	$4a_1$	-13.68	$4a_1$	-10.22
$1b_{2u}$	-16.16	$2e_g$	-14.50	$1b_{2g}$	-14.07	$1b_{1u}$	-13.73	$1b_{1u}$	-10.30
$1e_g$	-16.30	$1b_{2g}$	-14.85	$2e_g$	-14.28	$2e_g$	-14.08	$2e_g$	-10.69
$1a_{2u}$	-16.40	$1b_{2u}$	-16.30	$1b_{2u}$	-15.93	$1b_{2u}$	-15.56	$1b_{2u}$	-11.44
$(1e_u)$		$3a_1$	-16.37	$3a_1$	-16.02	$3a_1$	-15.67	$3a_1$	-11.67
$(1a_{1g})$ } -18.75		$1e_g$	-17.91	$1e_g$	-17.31	$1e_g$	-16.75	$1e_g$	-12.23
$(1b_{1g})$		$2a_1$	-23.73	$2a_1$	-23.42	$2a_1$	-23.09	$1e_u$	-18.28
		$1e_u$	-23.97	$1e_u$	-23.56	$1e_u$	-23.14	$2a_1$	-18.41
		$1a_1$	-24.54	$1a_1$	-24.09	$1a_1$	-23.68	$1b_{1g}$	-19.09
		$1b_{1g}$	-24.95	$1b_{1g}$	-24.47	$1b_{1g}$	-24.00	$1a_1$	-20.34

13 molecular orbitals as follows:

$$(1a_{2u})^2(1e_g)^4(1b_{2u})^2(1b_{1u})^2(2e_g)^4(2a_{2u})^2(2b_{2u})^2(3e_g)^4$$

$$(1a_{1u})^2(3a_{2u})^2 .$$

If we apply Mulliken's population analysis [10] to the wave function representing this electronic configuration, we obtain the following charge distribution:

$$N^{1.60} \; C^{0.95} \; C'^{0.95} \; C''^{1.03} .$$

The charge distribution suggests that the nitrogen atoms attract electrons from the carbon atoms but the degree is very small, and the whole molecule is almost homo-polar.

For ferrous porphyrin, the degree of mixing of the iron orbitals in the molecular orbitals is of some interest. In Table VI, the atomic populations are given for the molecular orbitals which have more than 10 o/o Fe 3d population.

The molecular orbitals which have the largest contribution of Fe 3d atomic orbitals are

$$2b_{1g} \sim 3d_{x^2-y^2},$$

$$6a_1 \sim 3d_{z^2} ,$$

$$4e_g \sim 3d_{xz} , 3d_{yz} ,$$

and $\quad 1b_{2g} \sim 3d_{xy} .$

They are indicated so in Figure 3. There is one exception. In the case of the point charge field, $5e_g$ instead of $4e_g$ has the largest $3d_{xz}$, $3d_{yz}$ character.

The order of the orbital energies ε of these orbitals, namely

$$\varepsilon(1b_{2g}) < \varepsilon(4e_g) < \varepsilon(6a_1) < \varepsilon(2b_{1g}) ,$$

is in agreement with the order indicated by electron spin resonance experiment on ferrite complexes. [11] However, the calculated difference between these levels is much too big in comparison with the values obtained by

TABLE VI   Atomic population for some molecular orbitals.

i) No external field

Atom MO	Fe(3d)	Fe(4s, 4p)	4Nσ	4Nπ	4C	8C'	8C"	N'
$2b_{1g}$	0.821	-	0.179	-	-	-	-	-
$6a_1$	0.848	0.029	0.069	0.000	0.001	0.000	0.000	0.053
$4e_g$	0.429	-	-	0.247	0.001	0.090	0.233	-
$2e_g$	0.114	-	-	0.004	0.177	0.334	0.371	-
$1b_{2g}$	1.000	-	-	-	-	-	-	-
$1e_g$	0.375	-	-	0.579	0.001	0.044	0.001	-
$1a_1$	0.127	-0.008	0.573	0.000	0.000	0.000	0.000	0.307
$1b_{1g}$	0.179	-	0.821	-	-	-	-	-

(ii) Dipolar field of 0.5 a.u.

Atom MO	Fe(3d)	Fe(4s, 4p)	4Nσ	4Nπ	4C	8C'	8C"	N'
$2b_{1g}$	0.830	-	0.170	-	-	-	-	-
$6a_1$	0.862	0.032	0.060	0.000	0.000	0.000	0.000	0.045
$4e_g$	0.462	-	-	0.190	0.001	0.144	0.203	-
$1b_{2g}$	1.000	-	-	-	-	-	-	-
$1e_g$	0.321	-	-	0.616	0.002	0.058	0.003	-
$1a_1$	0.111	-0.007	0.477	0.000	0.000	0.000	0.000	0.420
$1b_{1g}$	0.170	-	0.830	-	-	-	-	-

TABLE VI   (cont.)

(iii)   **Dipolar field of 1.0 a.u.**

MO \ Atom	Fe(3d)	Fe(4s,4p)	4Nσ	4Nπ	4C	8C'	8C"	N'
$2b_{1g}$	0.838	-	0.162	-	-	-	-	-
$6a_1$	0.873	0.035	0.052	0.000	0.000	0.000	0.000	0.039
$5e_g$	0.174	-	-	0.121	0.285	0.153	0.266	-
$4e_g$	0.442	-	-	0.120	0.013	0.213	0.211	-
$1b_{2g}$	1.000	-	-	-	-	-	-	-
$1e_g$	0.272	-	-	0.646	0.004	0.074	0.005	-
$1b_{1g}$	0.162	-	0.838	-	-	-	-	-

(iv)   Point charge of -1.0 a.u.

MO \ Atom	Fe(3d)	Fe(4s,4p)	4Nσ	4Nπ	4C	8C'	8C"	N'
$2b_{1g}$	0.844	-	0.156	-	-	-	-	-
$6a_1$	0.890	0.033	0.049	0.000	0.000	0.000	0.000	0.028
$5e_g$	0.522	-	-	0.156	0.154	0.035	0.133	-
$4e_g$	0.165	-	-	0.004	0.136	0.362	0.334	. -
$1b_{2g}$	1.000	-	-	-	-	-	-	-
$1e_g$	0.177	-	-	0.627	0.016	0.141	0.038	-
$1b_{1g}$	0.156	-	0.844	-	-	-	-	-

analysis of observed g tensor of ferrihaemoglobin aside. [12] For example, the calculated value of $\mathcal{E}\ (4e_g) - \mathcal{E}\ (1b_{2g})$ is 2.5 eV while Griffith's estimate is only about 0.2 eV.

It is apparent in Figure 3 that the orbital energies of the four orbitals of strong Fe character are more sensitive to the external field strength than the energy of the other molecular orbitals. This is quite natural since the Fe atom is the nearest to the source of the external field. However, both the energy differences between these levels and the percentage of Fe AO's in the orbitals do not change very much when the dipole is increased from 0 to 1 a.u. (about 2.5 Debye) or even for the case when a point charge increases from 0 to 1 a.u.

5.2. Electronic configuration and charge distribution of the low-spin state

For the low-spin state of ferro-porphyrin (with $S = 0$) , the electrons occupy the lowest 21 molecular orbitals as follows:

$$(1b_{1g})^2\ (1a_1)^2\ (1e_u)^4\ (2a_1)^2\ (1e_g)^4\ (3a_1)^2\ (1b_{2u})^2$$

$$(2e_g)^4\ (1b_{2g})^2\ (1b_{1u})^2\ (4a_1)^2\ (2b_{2u})^2\ (3e_g)^4\ (5a_1)^2$$

$$(1a_{1u})^2\ (4e_g)^4\ .$$

This configuration yields, by the population analysis, [10] the charge distributions which are given in Table 7. These, except for the point charge case, are reasonably close to our starting assumption about the formal charge, namely $Fe^{2.0+}\ N^{0.5-}$. In the case of the point charge of -1 a.u., its effect is so big that electrons are repelled from the central Fe atom to the peripheral carbon atoms, and the formal charge on the Fe atom is as great as +4.0 . As no stable ferrous complex with a negative ion at the sixth coordination position is known, an effort to make the calculation consistent in the charge distribution is not attempted.

TABLE VII   Charge distribution of ferro-porphyrin in the low-spin state. The values in parentheses are the formal charges.

	No external field	D = 0.5 a.u.	D = 1.0 a.u.	P = -1.0 a.u.
C"	1.03 (-0.03)	1.05 (-0.05)	1.07 (-0.07)	1.20 (-0.20)
C'	0.88 (0.12)	0.89 (0.11)	0.92 (0.08)	0.94 (0.06)
C	1.01 (-0.01)	1.02 (-0.02)	1.05 (-0.05)	1.22 (-0.22)
N	3.66 (-0.66)	3.64 (-0.64)	3.61 (-0.61)	3.53 (-0.53)
Fe	6.16 (1.84)	5.93 (2.07)	5.54 (2.46)	3.97 (4.03)
N'	1.91 (0.09)	1.92 (0.08)	1.94 (0.06)	1.97 (0.03)

5.3. Electronic configuration of the high-spin state

For the high spin state (with $S = 2$), we must have four singly-occupied orbitals. The sum of orbital energies is higher than that in the low-spin state, and the first stabilizing factor we can think of is the exchange interaction. Then the singly-occupied orbitals should be fairly localized around the Fe atom. The following configuration suggests itself

$$\cdots \ (1a_{1u})^2 (4e_g)^2 (6a_1)(2b_{1g}) \ . \qquad *)$$

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*)   For the case of the point charge,

$$\cdots \ (1a_{1u})^2 (5e_g)^2 (6a_1)(2b_{1g})$$

would be the configuration, but we shall not discuss it because of its inconsistency in charge distribution with the starting model.

The charge distributions obtained from the above configuration are given in Table VIII. The computed charge distribution is not as close to the starting charge distribution as it was in the case of the low-spin state. We should repeat the calculation starting from a new charge distribution something like $Fe^{1.2+} N^{0.5-} C'^{0.1+}$. Then we could obtain new orbitals and their orbital energies and see how much they are different from those in the low-spin case. We have not repeated the calculation, however, because the dependence of the molecular orbitals and their energies on the spin-state is caused also by electron-electron interaction which is not explicitly taken into account in the Hückel method.

TABLE VIII   Charge distribution of ferro-porphyrin in the high-spin state. The values in parentheses are the formal charges.

	No external field		D = 0.5 a.u.		D = 1.0 a.u.	
C″	0.97	(0.03)	1.00	(0.00)	1.02	(-0.02)
C′	0.86	(0.14)	0.86	(0.14)	0.86	(0.14)
C	1.01	(-0.01)	1.02	(-0.02)	1.04	(-0.04)
N	3.60	(-0.60)	3.60	(-0.60)	3.60	(-0.60)
Fe	7.00	(1.00)	6.73	(1.27)	6.40	(1.60)
N′	1.96	(0.04)	1.97	(0.03)	1.98	(0.02)

The orbital energy differences (cf. Table V) $\varepsilon(6a_1) + \varepsilon(2b_{1g}) - 2\varepsilon(4e_g)$ are 4.5 eV, 5.2 eV and 5.9 eV for D = 0, 0.5, 1.0 a.u., respectively. It seems not unreasonable to suppose that $4.5 \sim 6$ eV could be gained from the electron interaction energy in going from the low-spin to the high-spin state. To settle this point, as well as to obtain better molecular orbitals, it is necessary to apply a method, such as Pariser-Parr-Pople's [13], in which the Coulomb repulsion between electrons is explicitly taken into account.

It may be worth mentioning the orbital energy difference $\varepsilon(6a_1) + \varepsilon(2b_{1g}) - 2\varepsilon(4e_g)$ is bigger when the dipolar field strength D is greater. As there is no big change in the iron AO persentages of the three molecular

orbitals $6a_1$, $2b_{1g}$, and $4e_g$ when D increases from 0 to 1 a.u. (see Table VI), there should not be much change in the electron interaction energy. It looks, therefore, like the high-spin state is more unstable when the dipolar field is greater. However, ferrohemoglobin (with the water molecule as the sixth ligand) is known to be in the high-spin state while oxygenated hemoglobin (with the oxygen molecule, which has only an induced dipole [*], as the ligand) is in the low-spin state. Thus the computed result contradicts the experimentally known fact. This might suggest that there is a weak chemical bond between O_2 and haem and that the interaction is not essentially electrostatic.

5.4. Spectrum

Iron-porphyrin complexes show either one or two bands of moderate intensity in their visible spectra in the region 6300 Å (~ 2.0 eV) to 5000 Å (~ 2.5 eV) and an extremely strong band, called the Soret band, at about 4000 Å (~ 3.0 eV). Thus HbO_2, HbH_2O and even metal-free porphyrin have Soret peaks around 4000 Å.

The simple Hückel method employed here is known to be not reliable in discussing spectra. Nevertheless we try to see what we can say about the spectra from the results of the present calculations.

We assume that the Soret band for metal-free porphin is assigned to the transitions from the ground state to two excited configurations as follows: in one an electron is excited from $3a_{2u}$ to $4e_g$, in the other from $1a_{1u}$ to $4e_g$ [14]. For iron-porphyrin, then, it is natural to assign the Soret band to the transitions $5a_1 \rightarrow 5e_g$ and $1a_{1u} \rightarrow 5e_g$, since $5a_1$, $1a_{1u}$ and $5e_g$ correspond to $3a_{2u}$, $1a_{1u}$ and $4e_g$ in porphin, respectively. We see this not only from Figure 3, but also from Table IX which shows the atomic populations of these orbitals.

The differences between the orbital energies of these two configurations $\mathcal{E}(5e_g) - \mathcal{E}(1a_{1u})$ and $\mathcal{E}(5e_g) - \mathcal{E}(5a_1)$ are listed in Table X. This table shows that these orbital energy differences are insensitive to the dipolar field strength. There is a suggestion that the inter-configuration matrix element is

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[*]   The effect of a quadrupole is examined and found to be very small for a reasonable range for the strength of the quadrupole field.

TABLE IX   Atomic populations of some of the highest occupied and lowest unoccupied molecular orbitals.

(i) $4e_g$ (porphin) and $5e_g$

		4N	4C	8C'	8C"	Fe
porphin		0.078	0.362	0.244	0.316	-
iron-porphyrin	no external field	0.075	0.305	0.245	0.320	0.056
	D = 0.5 a.u.	0.094	0.301	0.208	0.301	0.095
	D = 1.0 a.u.	0.121	0.285	0.153	0.266	0.174

(ii) $1a_{1u}$

		4N	4C	8C'	8C"	Fe
porphin		-	-	0.724	0.276	-
iron-porphyrin	no external field	-	-	0.700	0.300	-
	D = 0.5 a.u.	-	-	0.694	0.306	-
	D = 1.0 a.u.	-	-	0.688	0.312	-

(iii) $3a_{2u}$ (porphin) and $5a_1$

		4N	4C	8C'	8C"	Fe	N'
porphin		0.152	0.632	0.061	0.156	-	-
iron-porphyrin	no external field	0.029	0.543	0.074	0.353	0.000	0.000
	D = 0.5 a.u.	0.035	0.556	0.076	0.331	0.001	0.000
	D = 1.0 a.u.	0.044	0.570	0.078	0.307	0.001	0.000

TABLE X $\quad\quad \varepsilon(5e_g) - \varepsilon(1a_{1u})$ and $\varepsilon(5e_g) - \varepsilon(5a_1)$ $\quad\quad$ (in eV).

	iron-porphyrin			porphin	
	no external field	D = 0.5 a.u.	D = 1.0 a.u.		
$\varepsilon(5e_g) - \varepsilon(1a_{1u})$	1.85	1.91	2.01	$\varepsilon(4e_g) - \varepsilon(1a_{1u})$	2.13
$\varepsilon(5e_g) - \varepsilon(5a_1)$	2.07	2.16	2.19	$\varepsilon(4e_g) - \varepsilon(3a_{2u})$	1.68

roughly constant for all porphins [14]. If we assume this, Table X indicates that the peak of Soret band is insensitive to the external field or the ligand at the sixth coordination position, in accordance with the experimental observation.

The inter-configuration mixing matrix element of 0.42 eV was used by Gouterman [14]. This value and the calculated orbital energy differences give the peak of Soret band of about 2.5 eV ($\sim$ 4960 Å), which is too big by 0.5 eV. However, the agreement is as good as we could expect in the simple Hückel method [*].

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[*] As the system is large and all the molecular orbitals involved in the transitions are spread over the porphin ring, we need not worry too much about a singlet-triplet splitting. The exchange integrals between these orbitals should be fairly small.

6. A DIFFICULTY WITH FERRIC IRON-PORPHYRIN

As was shown in Table VII, we obtained a charge distribution which is reasonably close to the starting model $Fe^{2+} N^{0.5-}$ for the ferrous iron-porphyrin in the low-spin state.

We have failed to obtain this consistency for the ferric iron-porphyrin. By starting from the model $Fe^{3+} N^{0.5-}$, all the orbitals with strong Fe 3d character turn out to have much too low energies. The resulting formal charge on Fe is nearly zero. By starting from the model $Fe^{2+} N^{0.25-}$ instead, the orbitals of strong iron character still come out much too low.

If we regard the ferric complex as the ferrous complex minus an electron in the highest occupied orbital, we arrive at the following model:

$$N^{'0.1+} Fe^{2.5+} N^{0.6-} C^{'0.1+} \qquad \text{(an electron missing from } 4e_g) .$$
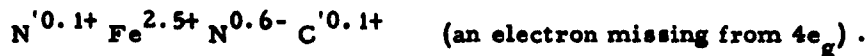
This model indicates that the electron removed in forming the ferric complex mainly comes from C' carbons.

If we speculate about the ferric complexes in the high-spin state, the above models lead to a picture in which unpaired electrons are fairly delocalized. Then the problem immediately arises; what is the stabilizing factor for the high-spin state, as the exchange interaction should be small?

On the other hand, if we assume the unpaired electrons are localized around the Fe atom, we have to explain why an electron can be taken away only from the Fe atom (without disturbing the balance between the Fe atom and the porphin ring), when the ferrous complex is oxidized.

It would be extremely nice if we could find out the distribution of these unpaired electrons in the complex from some experiment, such as a double resonance experiment.

APPENDIX I

Symmetry Orbitals

The co-ordinate system and the numbering of atoms in the molecular plane are shown in Figure 2.

(i)   Orbitals of the π-character

A_{1u}	C' 2pπ	1 - 2 + 3 - 4 + 5 - 6 + 7 - 8
	C" 2pπ	1 - 2 + 3 - 4 + 5 - 6 + 7 - 8
A_{2u}	Fe 4pz	
	N 2pπ	1 + 2 + 3 + 4
	C 2pπ	1 + 2 + 3 + 4
	C' 2pπ	1 + 2 + 3 + 4 + 5 + 6 + 7 + 8
	C" 2pπ	1 + 2 + 3 + 4 + 5 + 6 + 7 + 8
B_{1u}	C 2pπ	1 - 2 + 3 - 4
	C' 2pπ	1 + 2 - 3 - 4 + 5 + 6 - 7 - 8
	C" 2pπ	1 + 2 - 3 - 4 + 5 + 6 - 7 - 8
B_{2u}	N 2pπ	1 - 2 + 3 - 4
	C' 2pπ	1 - 2 - 3 + 4 + 5 - 6 - 7 - 8
	C" 2pπ	1 - 2 - 3 + 4 + 5 - 6 - 7 - 8
E_g	Fe $3d_{xz}$, ($3d_{yz}$)	
	N 2pπ	2 - 4, (1 - 3)
	C 2pπ	1 + 2 - 3 - 4, (1 - 2 - 3 + 4)
	C' 2pπ	2 + 3 - 6 - 7, (1 - 4 - 5 + 8)
	C' 2pπ	1 + 4 - 5 - 8, (2 - 3 - 6 + 7)
	C" 2pπ	2 + 3 - 6 - 7, (1 - 4 - 5 + 8)
	C" 2pπ	1 + 4 - 5 - 8, (2 - 3 - 6 + 7) .

Here   C' 2pπ 1 - 2 + 3 - 4 + 5 - 6 + 7 - 8, for example, means

$$\psi(A_{1u}) = N \{ (2p\pi)_{C'1} - (2p\pi)_{C'2} + (2p\pi)_{C'3} - (2p\pi)_{C'4} + (2p\pi)_{C'5}$$

$$- (2p\pi)_{C'6} + (2p\pi)_{C'7} - (2p\pi)_{C'8} \} ,$$

with a suitable normalization constant N .

(ii)   **Orbitals of the σ-character**

A$_{1g}$ Fe   3d$_{z^2}$

Fe   4s

N   σ $1 + 2 + 3 + 4$

B$_{1g}$ Fe   3d$_{x^2-y^2}$

N   σ $1 - 2 + 3 - 4$

B$_{2g}$ Fe   3d$_{xy}$

E$_u$ Fe   4px, (4py)

N   2-4, (1-3)

APPENDIX II

**Matrix elements of the potentials due to a
point charge, a dipole, and a quadrupole**

We denote the radial part of an atomic orbital by $R_{n\ell}(r)$, and
introduce the following integrals:

$$(k)_{\ell\ell'} = \frac{Ze}{R}\left\{\int_0^R R_{n\ell}\,R_{n'\ell'}\,(r/R)^k\,r^2\,dr + \right.$$

$$\left. + \int_R^\infty R_{n\ell}\,R_{n'\ell'}\,(R/r)^{k+1}\,r^2\,dr\right\} \quad (A1)$$

for the point charge case,

$$(k)_{\ell\ell'} = \frac{\mu}{R^2}\left\{-(k+1)\int_0^R R_{n\ell}\,R_{n'\ell'}\,(r/R)^k\,r^2\,dr\right.$$

$$\left. + k\int_R^\infty R_{n\ell}\,R_{n'\ell'}\,(R/r)^{k+1}\,r^2\,dr\right\} \quad (A2)$$

for the dipole case.

By using them, the matrix elements can be expressed as follows:

$$(\Delta |V| \Delta) = [0]_{\Delta\Delta},$$

$$(z |V| z) = [0]_{PP} + \frac{2}{5} [2]_{PP},$$

$$(x |V| x) = (y |V|y) = [0]_{PP} - \frac{1}{5} [2]_{PP},$$

$$(z^2 |V| z^2) = [0]_{dd} + \frac{2}{7} [2]_{dd} + \frac{6}{21} [4]_{dd},$$

$$(x^2-y^2| V|x^2-y^2) = (xy |V| xy) = [0]_{dd} - \frac{2}{7} [2]_{dd} + \frac{1}{21} [4]_{dd},$$

$$(yz| V | yz) = (zx |V| zx) = [0]_{dd} + \frac{1}{7} [2]_{dd} - \frac{4}{21} [4]_{dd},$$

$$(\Delta |V| z^2) = \frac{1}{\sqrt{5}} [2]_{\Delta d},$$

$$(\Delta |V| z) = \frac{1}{\sqrt{3}} [1]_{\Delta p},$$

$$(z |V| z^2) = \frac{2}{\sqrt{15}} [1]_{pd} + \frac{9}{7\sqrt{15}} [3]_{pd},$$

$$(x |V| zx) = (y |V| zy) = \frac{1}{\sqrt{5}} [1]_{pd} - \frac{3}{7\sqrt{5}} [3]_{pd}.$$

In the case of a quadrupole, we use

$$[k]_{ll'} = -(2k+1) \frac{Q}{R^3} \int_0^R R_{nl} R_{n'l'} (r/R)^k r^2 dr, \qquad (A3)$$

and

$$[k]_{ll'} = \frac{Q}{R^3} \Bigg[\int_0^R R_{nl} R_{n'l'} (r/R)^k r^2 dr$$

$$+ \int_R^\infty R_{nl} R_{n'l'} (R/r)^{k+1} r^2 dr \Bigg]. \qquad (A4)$$

The matrix elements are as follows:

$$(s \mid V \mid s) = [0]_{ss},$$

$$(z \mid V \mid z) = [0]_{pp} + \frac{2}{5} [2]_{pp} - \frac{2}{5} (2)_{pp},$$

$$(x \mid V \mid x) = [0]_{pp} - \frac{1}{5} [2]_{pp} + \frac{4}{5} (2)_{pp},$$

$$(y \mid V \mid y) = [0]_{pp} - \frac{1}{5} [2]_{pp} - \frac{2}{5} (2)_{pp},$$

$$(z^2 \mid V \mid z^2) = [0]_{dd} + \frac{2}{7} [2]_{dd} + \frac{6}{21} [4]_{dd} - \frac{2}{7} (2)_{dd} - \frac{36}{21} (4)_{dd},$$

$$(x^2-y^2 \mid V \mid x^2-y^2) = [0]_{dd} - \frac{2}{7} [2]_{dd} + \frac{1}{21} [4]_{dd} + \frac{2}{7} (2)_{dd} - \frac{6}{21} (4)_{dd},$$

$$(xy \mid V \mid xy) = (x^2-y^2 \mid V \mid x^2-y^2).$$

$$(yz \mid V \mid yz) = [0]_{dd} + \frac{1}{7} [2]_{dd} - \frac{4}{21} [4]_{dd} - \frac{4}{7} (2)_{dd} - \frac{6}{21} (4)_{dd},$$

$$(zx \mid V \mid zx) = [0]_{dd} + \frac{1}{7} [2]_{dd} - \frac{4}{21} [4]_{dd} + \frac{2}{7} (2)_{dd} + \frac{54}{21} (4)_{dd},$$

$$(x^2-y^2 \mid V \mid z^2) = - \frac{2\sqrt{3}}{7} (2)_{dd} + \frac{5\sqrt{3}}{7} (4)_{dd}.$$

$$(s \mid V \mid z^2) = \frac{1}{\sqrt{5}} [2]_{sd} - \frac{1}{\sqrt{5}} (2)_{sd},$$

$$(s \mid V \mid x^2-y^2) = \sqrt{\frac{3}{5}} (2)_{sd},$$

$$(s \mid V \mid z) = \frac{1}{\sqrt{3}} [1]_{sp},$$

$$(z \mid V \mid z^2) = \sqrt{\frac{3}{5}} [1]_{pd} + \frac{3\sqrt{3}}{7\sqrt{5}} [3]_{pd} - \frac{4\sqrt{5}}{7\sqrt{5}} (3)_{pd},$$

$$(z \mid V \mid x^2-y^2) = \frac{3\sqrt{5}}{7} (3)_{pd}$$

$$(x \mid V \mid zx) = \frac{1}{\sqrt{5}} [1]_{pd} - \frac{3}{7\sqrt{5}} [3]_{pd} + \frac{24}{7\sqrt{5}} (3)_{pd},$$

$$(y \mid V \mid yz) = \frac{1}{\sqrt{5}} [1]_{pd} - \frac{3}{7\sqrt{5}} [3]_{pd} - \frac{6}{7\sqrt{5}} (3)_{pd}.$$

The integrals $[k]_{ll'}$ and $(k)_{ll'}$ can be expressed in terms of elementary functions when the atomic orbitals involved are Slater functions and their principal quantum numbers are integers. When the principal quantum number is not an integer (e.g. for 4s and 4p), the integrals can be expressed in terms of incomplete gamma functions.

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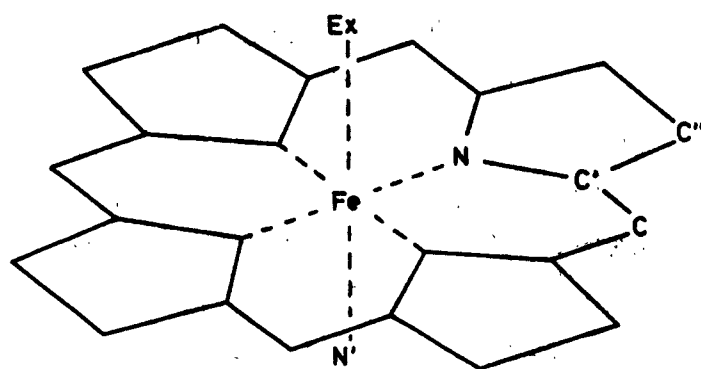
Figure 1   The skelton of iron-porphyrin   Ex
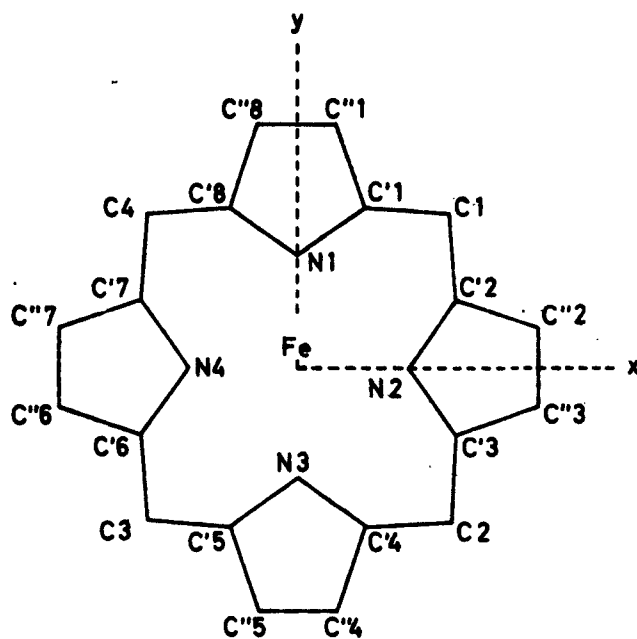indicates the position of a dipole or a
point charge.

Figure 2 The co-ordinate system and numbering of atoms.

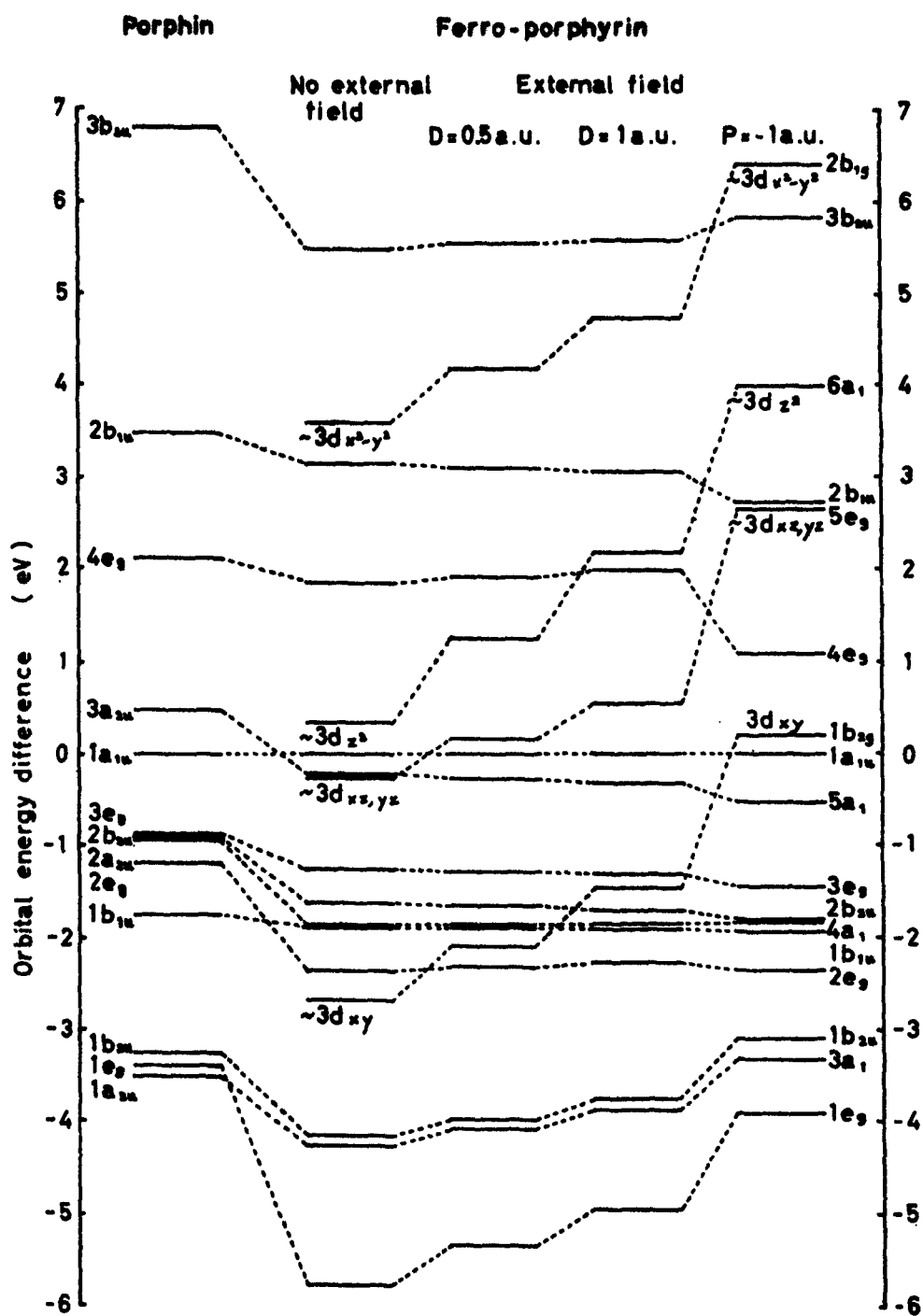**Figure 3   Energy levels of porphin and ferro-porphyrin.**

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ABSTRACT: The Hückel method is applied to the elec-
tronic structure of the iron-porphyrin complexes. The
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